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RESEARCH & DEVELOPMENT OF SEPARATORS
FOR SILVER OXIDE ZINC AND SILVER OXIDE
APPLICATION
Progress Report for the Period
June 2 7, 1963 - September 27, 1963

THE BORDEN CHEMICAL COMPANY
A Division of The Borden Company

GODFREY AVENUE AND LANGDON STREET

P. O. BOX 9524, PHILADELPHIA 24, PA.

FIRST QUARTERLY REPORT

To

National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

Covering

RESEARCH AND DEVELOPMENT OF
SEPARATORS FOR SILVER OXIDE-ZINC AND SILVER OXIDE-CADMIUM CELLS FOR
SPACECRAFT APPLICATION

T@ First Quarterly Report,

~~For the Period~~
June 27, 1963 - September 27, 1963

(NASA Contract No. NAS 5-3467)

1304005

The Borden Chemical Company
Central Research Laboratory
Philadelphia, Pa. #19124

H. E. Hoy T and
H. L. Pfluger   *November 15, 1963*   *26 p*

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TABLE OF CONTENTS

PROJECT PERSONNEL

In carrying out the experimental work on this project at The Borden Chemical
Company, the writers have been assisted by Dr. George Kitazawa, head of
physical testing laboratory, and by Messrs. Richard Trickey and J. Kaczaj
and Gregory Cali, assistant. In carrying out the sub-contract tests at
Burgess Battery Company, Dr. Howard Strauss has the assistance of
Messrs. Frederick A. Poss and Theodore A. Carus.

I. INTRODUCTION

This is the first quarterly report covering work during the reporting period of June 27, 1963 through September 27, 1963, on Contract No. NAS 5-3467 which was awarded to The Borden Chemical Company bh the National Aeronautics and Space Administration, Goddard Space Flight Center, on June 27, 1963. The Burgess Battery Company of Freeport, Illinois, is participating in this project as sub-contractor manufacturing test cells.

The objective of the contract is to develop new and improved membranes for separators in sealed silver oxide-zinc and silver oxide-cadmium cells for spacecraft application (1). Conventionally, the most generally used and most suitable membrane has proved to be regenerated cellulose or cellophane. Although such membranes conduct the current well and perform as barriers to soluble and colloidal silver and to zinc, they are prone to oxidation by silver oxide, and degradation by the electrolyte, leading to eventual failure of the membrane and short-circuiting.

The literature shows that other membrane types have been proposed and employed experimentally. These have often shown some resemblance to cellophane in such physical properties as swelling by the electrolyte, conductivity and barrier properties. We are attempting to investigate membrane types more broadly and systematically than has been done heretofore and to establish chemical and physical parameters, on the basis of which new more effective membranes might be fabricated. The present report deals chiefly with chemical variants of two polymer families, cellulose and polyvinyl alcohol.

II. SUMMARY

over

12/52

Films of diverse polymer types were prepared and screened as candidates for separators, using bench tests developed for this purpose. On the basis of the tests films of hydroxyethyl polyvinyl alcohol (HEPVA) and polyvinyl alcohol were submitted to Burgess Battery, our sub-contractor, for tests in cells.

Of the polymers screened to date only water-soluble or near water-soluble types have shown the order of conductivity of cellophane.

Resistance to oxidation under simulated cell conditions (silver oxide in 30% KOH) was measured by visual observation and by flex tests. These showed marked

deterioration of cellophane and excellent retention of flexibility by hydroxy-ethyl polyvinyl alcohol and polyvinyl alcohol. Methyl cellulose also resisted oxidation better than cellophane and may show sufficient promise to warrant trial in cells.

Tests are proceeding on the candidate polymers.

Study of proprietary copolymers containing carboxyl groups has been initiated.

AUTHOR

III. FUTURE PROGRAM

1) Needed refinements in screening tests are being made.

2) Screening of the polymers mentioned in this report will be completed and extended to include available water-soluble polymers.

3) Techniques of film making will be investigated aiming toward better control in obtaining perfect specimens.

4) Films from polyvinyl alcohol acetals of higher hydroxyl content than those reported to date will be prepared and tested in an effort to increase conductivity.

5) Films from copolymers of alkali-resistant monomers with acrylic or methacrylic acids will be prepared and screened, anticipating that carboxyl will contribute conductivity but with greater resistance to oxidation than hydroxyl.

IV. WORK PLAN

As agreed in conference with Mr. T. Hennigan and his staff and with Dr. Strauss, the separators for silver oxide-zinc batteries:

1) should withstand strong alkali (30% KOH)

2) should be an effective barrier to the zinc ions

3) should be resistant to oxidation

4) should have low electrical resistance

5) should be available dry

6) should be flexible

7) should be sealable, preferably by heat.

With these requirements in mind it is planned to screen a large number of polymer types according to their logical chemical and physical relationships, selecting the most likely candidates. These will be prepared in film form and sent to Burgess Battery Company for the construction of test cells for more definitive evaluation (1).

The screening conducted in this laboratory has been "bench scale" and the procedures have been set up after consultation with Dr. Howard Strauss. A brief description of these methods is given below. Detailed description of tests has been deferred for later reports in the anticipation that experience will lead to modifications and improvements.

1. <u>Insolubility in 30% and 40% KOH</u> — This is not a predictable property of films. As will be shown in Table II some water-soluble films are dissolved in KOH, while others maintain their integrity. A well dried film (minimum of 3 days) is immersed in the KOH solution for 96 hours and observations made.

2. <u>Electrolyte Absorption</u> — The rate and amount of electrolyte absorbed with time is measured by blotting and rapid weighing.

3. <u>Flexibility</u> — This test has been specified simply as the ability to make a sharp 180° bend. We have supplemented this original specification by use of the Shopper Tester to quantitatively measure changes in flexibility after exposure to KOH solutions and to the combination of silver oxide dissolved in KOH.

4. <u>Tensile Strength</u> — Measurement of tensile strength on Tinius Olsen Tester is measured after exposure to alkali electrolyte and silver oxide.

5. <u>Conductivity</u> — A cell was constructed according to the principle of Shair, Bruins and Gregor (11) to compare the resistance of membranes. At this time we are measuring resistance of the cell plus membrane so that only gross differences are found. Burgess Battery will make independent tests on films supplied by us.

6. <u>Oxidation Resistance</u> — We have chosen to study resistance to oxidation in 30% KOH solution in which silver oxide is dissolved and continuously dispersed. Since these conditions closely approximate those in the cell, it is hoped that they may correlate more directly than tests using other oxidation systems, such as permanganate or atmospheric oxygen (18).

7. <u>Zinc Ion Mobility Test</u> — The resistance cells are of the general design illustrated in Fig. 3 according to Dr. Strauss' recommendations. Two such cells constructed at Borden are in use and additional cells will be constructed at Burgess. A conductivity bridge, manufactured by Industrial Instruments, Inc., Cedar Grove, New Jersey, their Model RC 16B2 has been purchased for use in the resistance circuit at Burgess.

<u>CONSTRUCTION OF TEST CELLS</u> — A description of the normal 10 ampere-hour Ag_2O-Zn cell designed by Burgess and designated SS-5.5, follows. All components necessary for the construction of this cell are on hand at Burgess. Cycle life data is now being obtained to establish a level of performance. The Ag_2O-Zn cell is currently available for the evaluation of promising separator materials. Cycles with the HEPVA and PVAlc films have been started.

<u>General Design Parameters</u> of the Ag_2O-Zn cell SS-5.5 are as follows:

No. of Ag_2O Plates	6
No. of Zn Plates	7
Wt. Ag_2O/Plate	6.9 gm. (1.60 A.H.)
Wt. Zn/Plate	3.2 gm. (2.64 A.H.)
Ag_2O Plate Size	1.75 x 2.125 x 0.028 in.
Zn Plate Size	1.75 x 2.125 x 0.030 in.
Theoretical Cathode Ag_2O Capacity	9.65 A.H.
Theoretical Anode Capacity	18.45 A.H.
Separator	Single layer per plate side, 0.0027 in. Webril
Diaphragm	Five layers per plate side, 0.001 in. glycerine free cellulose

Individual Components of Ag_2O-Zn Cell SS-5.5 are as follows:

A. <u>Positive Plate</u> - The positive plate is fabricated and assembled in the cell in the discharged condition, i.e. as metallic Ag. The plate contains a support grid of Ag wire. Each plate contains 6.9 gm. Ag_2O or 1.60 ampere hours capacity. Plate formulation and fabrication techniques are considered proprietary information. The physical size of the positive plate is illustrated in Fig. 1.

B. <u>Negative Plate</u> - The negative plate is fabricated and assembled in the cell in the discharged condition, i.e. as ZnO. The plate contains a support grid of Ag wire. Each plate contains 3.2 gm. Zn of 2.64 ampere hours capacity. Plate formulation and fabrication techniques are considered proprietary information. The physical size of the negative plate is illustrated in Fig. 1.

C. <u>Terminal Piece</u> - The terminal pieces are fabricated from cold rolled copper and silver plated. The lead wires from the cell electrodes are threaded through the terminal pieces and soldered in place. An "O" ring is used to form a seal between the cell case top and the terminal piece.

D. <u>Cell Case</u> - The cell case, consisting of vent plug, case top and case body, are made of nylon. The physical size of the cell case is illustrated in Fig. 2.

SEPARATION SYSTEM

1. Diaphragm

   DuPont 193 PUDO, 0.001 inch thick regenerated cellulose, three (3) sheets 18 5/16" x 5 1/4" per cell.

2. Separator

   Webril, grade 1401, dynel fiber 0.003 inches thick, 37 gm/sq. yd. Seven (7) sheets 4 3/8" x 1 3/4" and six (6) sheets 5 1/4" x 1 3/4" per cell.

CONSTRUCTION of Ag_2O-Zn CELL SS-5.5 is as follows:

A. Positive and negative plates have a single layer of grade 1401 Webril on each side.

B. Positive plates are "U" wrapped in Dupont 193 PUDO 0.001 inch cellophane, five layers on each side.

C. A negative plate is placed on each side of all positive plates. Using six (6) positive plates and seven (7) negative plates the finished assembly contains thirteen (13) plates.

D. Terminal pieces are soldered to the terminal leads and the cell plate

assembly is placed in the cell case.

E. 30% KOH is added as the electrolyte.

All cell components are on hand. A sufficient number of cells has been assembled to test the design mechanically and electrochemically. Cycle life data is now being obtained to establish a level of performance.

Testing Schedule is as follows:

A. Construction:

1. Assemble cells in the discharged state.
2. Fill with electrolyte.
3. Allow to stand for 24 hours.

B. General Cycle:

1. Charge at C/20 amperes for 24 hours (total input 1.20 C ampere hours). (where C is the theoretical Ag_2O cell capacity in ampere hours.)
2. Allow to stand in the charged state for a fixed predetermined time.
3. Discharge at a constant drain rate to a terminal voltage of 1.0.
4. Allow to stand in the discharged state for 3-8 hours prior to recharging.

C. Four Conditioning Cycles:

1. Allow cells to stand in the charged state for 16 hours. Over weekends and holidays cells will stand in their charged state.
2. Cycle number one and two, discharge at a rate of C/5 amperes (about 5 hours).
3. Cycle number three, discharge at a rate of C/1 amperes (about 1 hour).
4. Cycle number four, discharge at a rate of C/0.2 amperes (about 12 minutes).
5. Following each discharge, cells will be recharged as described in B1.

D. Life Test Cycles:

1. Initiate following the four conditioning cycles.
2. Allow cells to stand in the charged state for 16 hours. Over weekends and holidays cells stand in their charged state.
3. All life test cycles are performed at a discharge rate of C/5 amperes. (about 5 hours).
4. Following each discharge, cells will be recharged as described in B1.
5. The criterion of failure for individual cells is their inability to deliver a capacity of more than 0.6 C.

E. Charge Retention Test Cycles:

1. Initiate following the four conditioning cycles.
2. Allow to stand in the charged state for 30 days.
3. Discharge at C/5 amperes (about 5 hours).
4. Allow to stand for 3 hours.
5. Recharge as described in B1.
6. Repeat A through E.
7. The criterion of cell failure is described in D5.
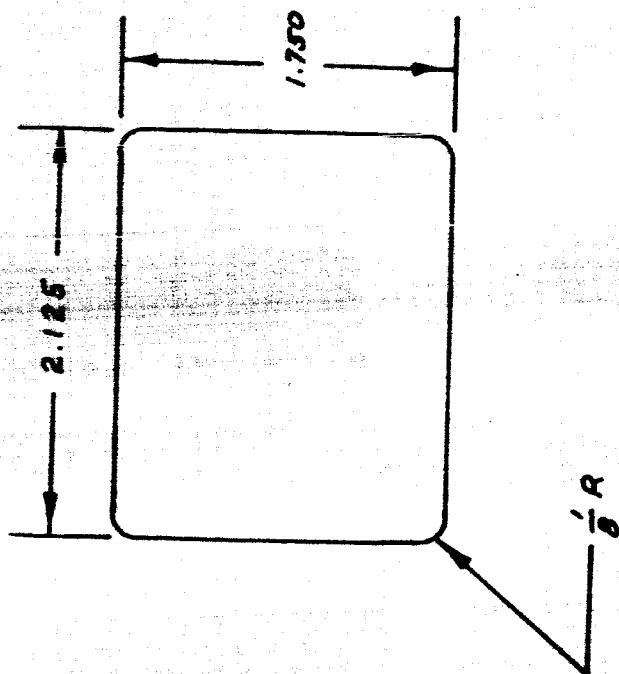
2.125

1.750

$\frac{1}{8}$ R

Fig. 1.

Fig. 2

3.675

3.375

2.110

0.850

UNLESS OTHERWISE SPECIFIED Inner Box Dimensions - ½" Wire Length - 1 64" All other Dimensions = 1/32".

① Fill Port
② S.S. Screen Electrode
③ End Plate
④ Electrolyte Chamber
⑤ Center Plate
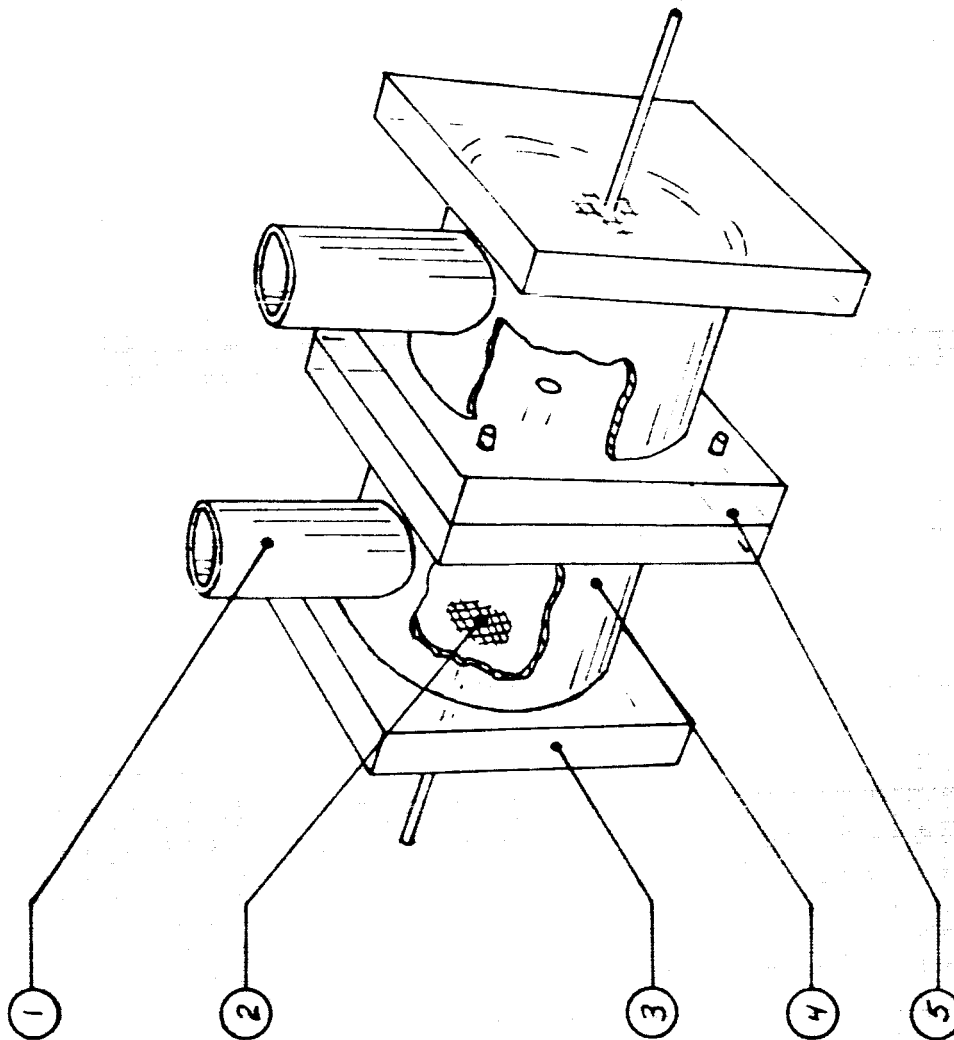
Fig. 3

UNLESS OTHERWISE SPECIFIED Inner Bar Dimensions - 1/64" Wire Length - 1/8" All other Dimensions ± 1/32"

V. HYDROXYETHYL POLYVINYL ALCOHOL (HEPVA) AND WATER-SOLUBLE POLYMERS:

The first promising film material which emerged from the preliminary screening tests was a Borden developed hydroxyethyl polyvinyl alcohol (HEPVA) which offered the advantages of flexibility and heat sealability. A large number of variants of this polymer were available from previous experimental work. HEPVA may be produced in a number of forms determined by (a) the molecular weight of the polyvinyl alcohol, (b) the number of residual acetate groups (from the parent polyvinyl acetate), (c) the amount and type of ethoxylation.   A large number of available proprietary films of this class (both commercial and experimental) were screened as to behavior in 30% KOH and as to resistance to oxidation by silver oxide in the presence of 30% KOH.

Of 75 films immersed in the KOH all maintained their integrity after 60 days. The first two films removed were washed in water and found to be insoluble. Since HEPVA is normally water-soluble it was first thought that the KOH had in some way promoted a cross-linking reaction and that the insolubility was a consequence of this cross-linking. As the other films were removed from the KOH, however, it was found that of the 75 films subjected to the treatment only five had become water-insoluble; the other 70 readily dissolved in water as all did in their original untreated form. An attempt was made to correlate the insolubilization with residual saponifiable, as shown in Table I.

TABLE I. - HEPVA and Polyvinyl Alcohol. Saponification Study

Sample *	Type and History	Water Soly. after KOH Soak	Free Acid meq/g	Saponification Value meq/g	.Sap.No.
79	HEPVA Film Commercial roll, unknown history	insol.	.024; .040 .041, .039	1.50; 1.54; 1.62; 1.63 1.60	90
48	HEPVA Film, Monosol	insol.	.60	1.89	105
9	HEPVA Film, unknown	insol.	.02	1.66	93
36	HEPVA Film from 60-98 Lemol-derived HEPVA (A)	insol.	.02	0.16	9
264-25	Fresh film from 30-98 Lemol-derived HEPVA (A)	insol.	.09	0.39	22
51	Film from 60-98-Lemol-derived HEPVA (A)	sol. *	.12 *	*	0.28 *	16
Lemol 50-98 PVAlc (Control)		-	.00	0.28	16
Lemol 42-88 PVAlc (Control)		-	.05	2.23	125

Note (A) LEMOL = Borden polyvinyl alcohol. The first figure refers to viscosity; the second is degree of hydrolysis of the polyvinyl acetate.

Other research in The Borden Company has indicated that HEPVA films are capable of insolubilization as a result of peroxide pickup on storage. Since KOH might be expected to promote the action of peroxides, it is quite likely that such action was responsible for the insolubilization of the five films in question.

The question remained as to why the other seventy samples of HEPVA maintained their integrity in concentrated KOH solution without losingtheir ability to dissolve subsequently in water. This was shown to be a simple matter of salting out. If HEPVA is dissolved in water, addition of strong KOH or solid KOH results in precipitation of the polymer. The precipitated polymer is in turn soluble in water. This is not unique to HEPVA, as is shown in Table II. The importance of this observation is that it opens up the investigation for battery separators film forming, water-soluble polymers which may not have been considered previously as possibilities. A number of water-soluble polymers have been cast into films and the films immersed in 30% and 40% KOH for observation, with the results shown below:

TABLE II. - Solubility of Water-Soluble Films in 30% KOH, 40% KOH (after 24 hrs.)

Polymer	Water	KOH 30%	KOH 40%
Methyl Cellulose	sol.	insol.	insol**
Hydroxyethyl Cellulose	sol.	sol.	sol.
Carboxymethyl Cellulose	sol.	sol.	sol.
Sodium alginate	sol.	sol.	insol.but weak
Polyvinyl Pyrolidone	sol.	insol.	insol.
Methocel H.G. *	sol.	insol.	insol.
Polyethylene Oxide ***	sol.	insol.	insol.
Polyvinyl Alcohol	sol.(hot)	insol.	insol.
HEPVA	sol.	insol.	insol.

*Dow 28-30% methoxyl, 7-12% hydroxy propyl
**Film removed after 48 hours appeared quite strong, more so than that subsequently tested after drying (Table III).
*** Union Carbide Polyox WSRN 80.

Referring to Tables III and IV, it can be seen that HEPVA exhibits conductivity comparable to cellophane and superior flexibility. Although it reacted readily with silver oxide (at about the rate of cellophane) the physical deterioration by silver oxide-KOH or by KOH alone was markedly less than that of cellophane. A sample was sent to Burgess for use in test cells.

VI. <u>POLYVINYL ALCOHOL (PVAlc)</u> - itself is an example of a water-soluble polymer which is insoluble in concentrated KOH. Its insolubility in KOH has been previously exploited in cells. It has been used in film form for separators (14) or in compound membranes (11), as well as in pastes for the silver oxide of that electrode (13). In our tests conductivity and flexibility were good. PVAlc readily reacted with silver oxide (about the rate of cellophane) but unlike cellophane, no extensive degradation occurred. As stated in note K of Table V, some stretching occurred in 30% KOH. The relatively low conductivity in 40% KOH requires confirmation inasmuch as the test sample was inordinately thick and may have been tested before it reached equilibrium with the electrolyte.

A sample of film was sent to Burgess for use in test cells.

VII. <u>METHYL CELLULOSE</u>

Our tests on this material showed that it was oxidized by silver oxide to a lesser degree than was cellophane and that it survived this oxidation much better in respect to maintaining the original physical condition. The initial flexibility and strength of the film was inferior to cellophane. Improved technique in the preparation of films could lead to improved physical properties. Conductivity was somewhat inferior to cellophane, apparently much inferior in 40%, but further refinement of test methods may alter this picture. Because of oxidation resistance superior to cellophane methyl cellulose may be considered a potential candidate. Improved films are required.

VII. DISCUSSION

Two main trends have been indicated: (1) The separator material needs to have a rather high degree of hydrophilicity and (2) polymers with a multiplicity of hydroxyl groups appear to be prone to attack by silver oxide. If the hydrophilicity necessary for conductance is imparted by hydroxyl groups, and oxidative attack is at the hydroxyl, some degradation would be inevitable.

Two families of polymers were subjected to prolonged room temperature oxidation by silver oxide in 30% KOH. The degree of silver deposition was judged by visual observation (as silver is deposited and the color progresses from no color (0) to light brown (1), to dark brown (2), to black (3), to a mirror (4), to a silvery deposit (5), which may be easily scraped off the surface). On this basis the two families of polymers showed the following rating after 96 hours in a stirred suspension of Ag_2O in 30% KOH:

Cellophane	4	Polyvinyl Alcohol	5
Methyl cellulose	3	Formal of PVAlc	1
Ethyl cellulose	0	Butyral of PVAlc	0
		Hydroxyethyl PVAlc	4

It is seen that blocking the hydroxyls in the parent polymers decreased the oxidation in both cases except where the blocking group itself furnished hydroxyls (hydroxyethyl polyvinyl alcohol).

In a preliminary study of the mechanism of oxidation of polyvinyl alcohol a 5% aqueous solution was rigorously oxidized with 2/3 mole of silver oxide per hydroxyl group. Complete reduction of the silver oxide occurred. Development of ketonic carboxyl (by hydroxyl amine and I.R.) was shown as well as carboxyl, presumably the oxidative scission of the enolic form of the group

$$(CH_2 - \underset{\underset{O}{\|}}{C}) \qquad (-CH = \underset{\underset{OH}{|}}{CH} -)$$
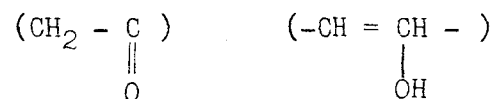
Despite these changes a film cast from the oxidized polyvinyl alcohol showed good strength. The hypothesis that the hydroxyl is the point of oxidation attack is tempting but it should be noted that the degree of silver deposit correlated also with hydrophilicity so that solubility of the silver oxide in the film may be the controlling factor.

As a measurement of physical changes induced in the films by the action of (1) KOH, and (2) KOH + Ag_2O, films were treated as recorded in Table I and tested for the effect of these reagents on the flexibility. In the case of cellophane flexibility was lost even after 24 hours exposure to KOH only. After 24 hours stirring in KOH-Ag_2O the film became extremely brittle. (The observed holes are believed to have developed on handling the embrittled film, i.e., they were probably not

actually produced directly by the oxidation.) Polyvinyl alcohol and HEPVA films
did not lose measurable flexibility under these conditions even though both were
heavily coated with silver in that test. Methyl cellulose appeared to resist
oxidation better than cellophane but the intrinsic flexibility of methyl cellu-
lose films was not high. Butvar and Formvar films lost relatively little in
flexibility.

In these tests the films after reaction in KOH and Ag2O-KOH were stored in the
relatively dry atmosphere of the main laboratory. The tests of Table I were
carried out after storage at 50 RH for seven days, which has previously been
found the time necessary for right equilibration of HEPVA films. Before equili-
bration several of the films were quite brittle, become increasingly flexible
when stored in the physical testing lab where the RH is 50. There is some question
how these tests correlate with flexibility in the electrolyte at 30% KOH. Such a
direct test would be extremely difficult, but it is planned to test some films
immediately after removing from the electrolyte.

A new conductivity cell was constructed with a smaller opening between the two
halves (.201 inches diameter) in order to maximize differences among films. The
new cell, like the first one, showed no differences between cellophane, HEPVA and
PVAlc on the one hand and no membrane on the other. Nevertheless, valuable com-
parisons resulted as shown in Tables II and III. Of the new polymers tested only
methyl cellulose showed conductivity of the order given by cellophane. It will be
noted that for this film, conductivity was much lower in 40% than in 30% KOH.
This was true for polyvinyl alcohol as well. The values given must be accepted
with some reservation since test studies on equilibrating the membranes have not
been completed, and may lead to revised values. As examples, the conductivity of
cellophane in 30% KOH read .52 at zero minutes as well as at fifteen minutes.
In 40% KOH conductivity of the polyvinyl alcohol film reached 0.10 at 30 minutes
and was probably not at equilibrium then.

Further refinement of test procedures is needed. So far it appears that the only
candidates are of the water-soluble or near-water-soluble types.

Analytical Studies:

(1) Commercial acetals of polyvinyl alcohol do not include low acetal
polymers (high residual hydroxyl). Several were prepared and will be charac-
terized and tested.

(2) Co-polymers of methacrylic esters with monomers imparting flexibility could
conceivably be hydrolyzed to give carboxyl functions and requisite conductivity.
The hydrolysis by saponification of Dow's Zetafin, believed to be a copolymer of
ethylene and acrylate ester, was unsuccessful. Turning to a known homopolymer
as a model, polyethyl methacrylate, the saponification was studied. This polymer
was not attacked at all by 24 hour heating in conventional analytical techniques.

Substantial attack was achieved only by the following rigorous conditions:
Sodium was dissolved in glycol and the polymer heated with an excess in purified
butyl carbitol (solvent) at 208° C. for two hours. Saponifiable found – 5.97 meq./
gram. Calculated – 8.76 meq./gram. In view of the resistance to saponification
of the methacrylate, copolymers with vinyl acetate might be hydrolyzable to
hydroxyl-containing copolymers in which the acrylate moiety remains intact.

TABLE III. – Effect of KOH and Ag_2O on Membranes – Shopper Fold Tests

Code 389 –	Polymer	Thickness mils	Cycles	Type Break	Comments
12	Cellophane PUDO	)1.1	1954	ragged	Commercial film
		#1(1.1	1744	"	
		)1.1	1818	"	Clear and uniform
	Cellophane PUDO	#2(1.1	2181	"	
		)1.1	2129	"	
12K 24 hr.	Cellophane PUDO	1.2	425	"	
		1.1	526	"	
		1.1	459	"	
		1.1	569	"	
12A– 24 hr.	Cellophane PUDO	2.0	20	Shatter	Heavy silver coating – Sample had too many holes for further tests
35	PVAlc	3.5	5000	–	
35X–96 hr.	"	3.0	5000	–	
35A–96 hr.	"	4.5	5000	–	Heavy silver coating
9	HEPVA	0.7	Could not test (stretches)		
9K–64 hr.	"	0.7	3066	–	Broke in grip
	"	0.7	5000	–	
9A–64 hr.	"	0.8	5000	–	Heavy silver coating
29	Me Cellulose	1.6	550	ragged	
		1.6	185	sharp	
		1.6	104	broke in grip	
29K–96 hr.	" "	2.0	91	ragged	
		2.1	112	ragged	
		2.1	118	ragged	
		2.1	79	hole (?)	
29A–96 hr.	" "	2.3	126	uneven	Moderate silver coating
		2.4	133		
25	Formvar 7/95S	1.1	1103	ragged	
		1.1	1307	ragged	
25K–96 hr.	Formvar 7/95S	1.1	722	sharp	
		0.9	613	ragged	
		1.7	689	sharp	

(Table continued on following sheet)

TABLE III. – Effect of KOH and Ag₂O on Membranes – Shopper Fold Tests (CONTINUED)

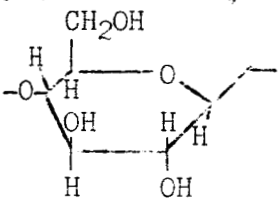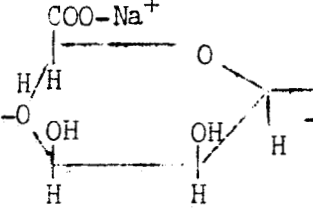| Code 389–	Polymer	Thickness mil	Cycles	Type Break	Comments
25A 96 hr.	Formvar	1.0	881	ragged	Very slight silver coating
26	Butvar B73	1.1 1.2	4238 7500	sharp	
26K–96 hr.	Butvar B73	1.1 1.1	3177 272	ragged tear	
26A–96 hr.	Butvar B73	1.3 1.4	1179 5000	ragged –	No silver coating
23	Elvax	1.0	could not test – stretches		
23K–96 hr.	Elvax	1.0	"	"	"
23A–96 hr.	Elvax	1.0	"	"	" No silver coating

Code Explanation:
   K = soaked in 30% KOH for the hours specified by the following number.
   A = soaked in a stirred suspension of Ag₂O in 30% KOH for the hours specified in the following number.

Condition of Exposure:
   Films covered with 30% KOH, blotted dry without washing. Conditioned at 73° F. at RH 50 for 7 days before flex test, same condition.
   For Ag₂O–KOH test 5 g. Ag₂O/liter 30% KOH, continuously stirred, films segregated from stirring mechanism. Dried and conditioned as above.

TABLE IV. - Electrical Conductivity in KOH. Cellulose and Derivatives
(cell constant with 1N KCl, 23° C.
K = A/1 - .0617 cm; hole 0.20 inches diameter)

Reference	Polymer	Groups attached to backbone	30% KOH	40% KOH
			Conductivity (Ohms^{-1} Cm^{-1})	
	Cell conductivity (no membrane)		.52	.46
	PUDO Cellophane	etc.	.52	.46
389-29	Methyl Cellulose C.P. (B)	−OMe	.32	*16 x 10^{-6}
389-44	Methocel HG 60 (C)	−OMe, −OCH$_2$CH$_2$CH$_2$OH	11 x 10^{-5}	12 x 10^{-5}
389-49-1	Ethyl Cellulose T100 (D)	−OEt		
389-49-2	Ethyl Cellulose G100 (E)	−OEt		
374-22	Carboxymethyl Cellulose (F)	−CH$_2$OCH$_2$COO− Na+	sol	sol
374-19	Hydroxyethyl Cellulose QP 5200 (G)	−OCH$_2$CH$_2$OH	sol	sol
389-24	Sodium Alginate (H)	− Etc.	sol	weakened

Notes: (A) Du Pont (no plasticizer)
(B) 29-33% methoxy
(C) Dow, 28-30% methoxyl, 7-12% hydroxypropyl
(D) Hercules 49% + ethoxyl
(E) Hercules 44.5-45.5% ethoxyl
(F) Hercules
(G) Union Carbide QP 5200
(H) Matheson, Coleman and Bell
* Less than this value (off scale)

TABLE V. – Electrical Conductivity in KOH, Polyvinyl Alcohol and
Derivatives. – (Hole 0.201 inches diameter, cell
constant with 1N KCl K = Λ/1 = .0617 cm)

Reference	Polymer,	Groups attached to backbone	30% KOH	40% KOH
			Conductivity Ohms^{-1} Cm^{-1}	
	Cell Conductivity (no membrane)		.52	.46
389-37	PVAlc $-CH_2-CH-CH_2CH-$ (A) OH OH		.52 (K)	.10
79	Hydroxyethyl Polyvinyl Alcohol (HEPVA) $-OCH_2CH_2OH$ (B)		.52	.46
389-25	Polyvinyl formal (C)	$-O-CH_2-O-$	$16 \times 10^{*-6}$	48×10^{-6}
389-26	Polyvinyl butyral (D)	$-O-CH-O-$ Pr	$16 \times 10^{*-6}$	16×10^{-6}

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Miscellaneous Polymers

Reference	Polymer		30% KOH	40% KOH
389-23-3	Copolymer of ethylene and acrylate (E)		$16^* \times 10^{-6}$	$16^* \times 10^{-6}$
389-23-1	Copolymer of ethylene and vinyl acetate (F)		$16^* \times 10^{-6}$	$16^* \times 10^{-6}$
389-36	Poly(methylvinylether maleic anhydride) (G)		brittle soluble films	
389-46	Polyvinyl Pyrolidone (H) $-CH-CH_2-$ N CH_2 C = O CH_2- CH_2		insol. but films too brittle to test	

Table V Notes:
(A) Borden's LEMOL 30-98
(B) Borden's LEMOFLEX. A commercial film hydroxyethyl content (assumed 26%), Sapon. No. 89.
(C) Shawinigan's Formvar 7/95S. 80% Formal as P.V.F.; 7-9% OH as PVAlc; 9-13% acetate as PVA.
(D) Shawinigan's Butvar B73. 80% butyral as P.V.B; 21% OH as PVAlc; 2.5% acetate as PVA.
(E) Dow's Zetafin
(F) du Pont's Elvax
(G) General Aniline's Gantrez AN
(H) General Aniline
(K) Softened and stretched at test area
 * Below 16×10^{-6} (off scale)

LITERATURE SURVEY:

The problem of zinc dendrites (trees) is a result of the partial solubility of the zinc on discharge of the cell. The zinc may dissolve in either of several forms, Zn^{++}, $ZnO_2^=$, $Zn(OH)_4^=$, etc. In a series of studies by Dirkse (2) the latter ionic structure is proposed. The ability of the zincate to produce supersaturated solution leads to migration through the separator system according to Rhyne (13).

Upon charging the cell, the zinc is redeposited on the anode, but it plates out at the location of the highest current density. Thus, there is a build-up of zinc at the location of highest current density. There is a build-up of zinc at edges and rough points on the electrode surface. In a mutiple plate battery, there is also a migration of zinc. This was studied by Palagyi (3) who built cells having 9 electrodes, including 4 silver oxide cathodes and 5 zinc anodes. The middle zinc electrode contained radioactive Zn^{65} isotope. The cells were assembled in 3 ways, normal dimensions, large dimensions (more electrolyte) and tight packing. Radioactive zinc reached all the nonlabelled zinc electrodes, and there was also some contamination of the silver plates. There was more contamination and a shorter cycle life in the loosely assembled cells having more electrolyte. These cells failed due to shedding and sludging of the zinc. The failure of the tightly packed cells was due largely to separator breakdown, with dissolution of silver oxide from the positive electrode and migration of silver towards the negative plates, and the formation of zinc trees ultimately causing a direct short.

Palagyi repeated this work using radioactive cathodes labelled with Ag^{110} isotope. The non-labelled electrodes were contaminated by the isotope to a smaller degree than in the zinc isotope experiments. Radioactive silver reached all the electrodes in only 1 cell out of 20 examined, and 5 of the 20 showed no contamination at all. Unlike the zinc isotope experiment, contamination was greatest in the tightly assembled cells, where the small volume of electrolyte minimizes solubility.

Palagyi also found that during storage, cells stored in the charged state showed greater contamination of non-labelled electrodes, and furnished fewer cycles after storage, then did cells stored in the discharged state.

Howard (5) states that the zinc content of the electrolyte is more than 3000 times the silver content. He found that 95% of the dissolved zinc goes into solution within 24 hours.

The silver oxide electrode and the electrochemistry of silver and its oxides has been studied by several investigators in great detail in recent years. Ruetschi (6) used a-c polarographic cell to study the solubility of silver oxides in KOH. When KOH solution is saturated with either AgO or Ag_2O, the same soluble silver species (monovalent) is obtained. No divalent silver could be detected in the solution. Ruetschi believes that any divalent oxide which may dissolve is rapidly decomposed to the monovalent form. This decomposition was studies by oxygen evolution, and was found to be light sensitive.

The exact structure of the oxides of silver is a matter of controversy. Neutron diffraction studies have established that the divalent oxide is AgO, and not a silver peroxide, Ag_2O_2 as it was formerly assumed (7).

A higher oxide of silver, Ag_2O_3, has been reported to be extremely unstable (8). Palagyi (9) states that only these three oxides (Ag_2O, AgO, Ag_2O_3) exist, contrary to earlier reports of Ag_4O and Ag_4O_3. He used X-ray diffraction to identify the species. Methods of preparation for the three oxides in high purity are given. An excellent review of the silver oxide electrode has been prepared by Dirkse (10).

Although cellophane is currently the most widely used separator for the Ag_2O-Zn system because of its low resistance to electrolyte and impermeability to zinc, a great many papers and patents have suggested improved cellulosic or non-cellulosic substitutes. A complete literature survey on this topic was compiled in the NASA project reports on battery separators at Electric Storage Battery Co. A complete set of these reports was given us by Mr. Hennigan and it is felt that a repetition of this literature survey would be unnecessary. The E.S.B. Literature survey should be considered a part of the background of this project. However, a few of the proposed separator materials are of interest.

A series of papers from Brooklyn Polytech. describes the preparation of ion exchange type separator membranes (11). Several of these membranes are commercially available from Gelman Instrument Co., Chelsea, Michigan under the trade name "Polypor". Non-ionic Polypor is a solution of polyvinyl alcohol and Dynel in DMF, used to impregnate a woven Nylon base. A pore diameter of 2100A is claimed. WA Polypor (weak acid ion exchange) and WB Polypor (weak base ion exchange) comprise an ion exchange resin plus Dynel, again dissolved in DMF. Pore diameter are said to be 500-1000A.

In a 152 page report containing 232 references Rhyne (13) investigated the Polypor membranes in conjunction with cellulosic types and reports negligible silver penetration of the ester layer when Polypor WA was used next to the positive plate. Keralla (16) later characterized this as a porous non-reactive layer. However, our interpretation of Rhyne's work was that KOH concentration was a far more important factor than membrane type in restricting silver loss. At 40% KOH loss of silver was only one-third that at 30% using cellophane as separator. At 40% differences among membrane systems appeared to be nil within experimental variation. (Possibly, as a result of this work, Keralla used 40% KOH in his investigations (16). Fibrous sausage casing (Visking) was reported by Rhyne to be the most effective barrier against zinc. Evidence was claimed that inclusion of polyethylene oxide in the negative restricts the migration of the zinc and further inhibits penetration of separator by the zinc.

The relationship of pore size to barrier properties is not at all clear from the literature, possibly because the investigators up until recent work by Electric Storage Battery Co. (18) have not taken into account the effect of swelling of the membrane in the particular concentration of KOH to which it will be subjected.

Although their work was on separators for sealed nickel-cadmium batteries a paper by Seiger et al (17) seems pertinent in that it calls attention to the desirability of high electrolyte absorption and retention by the separator. Four times the dry weight was recommended and 30% retention of electrolyte after acceleration (rate not stated). Kryukova (14) hints that an unspecified surfactant in very small amounts in a cellulosic membrane completely inhibits the penetration by zinc and presents some artistic drawings to prove his point. Like Rhyne (13) he pictures the penetration as mechanical (puncturing) rather than electrical, an argument which Dr. Strauss disputes. According to Strauss' analysis pentration occurs only at a hole or weak spot which affords a higher density and this promotes growth along this path. Kryukova used polyvinyl alcohol film as a control, claiming it offered no resistance whatever to dendrite growth.

This is at variance with Bieber (15) and others who have reported good cycle life for polyvinyl alcohol-based membranes. Keralla (16) reported increased cycle life by the use of polyvinyl alcohol as a binder for the zinc electrode.

Bruins (12) claims that these separators work as well as cellophane which has a pore diameter of 30 Å. However, microporous PVC (Synpor) separators, with a pore diamater of 50,000-100,000 are not effective. Bruins concludes that his ion exchange separators act as a barrier to the migration of colloidal silver. He states that a good separator must have a pore structure capable of acting as a colloidal filter. Bruins also describes an acid-hydrolyzed polyvinyl butyral membrane, having a pore size of 60 Å.

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